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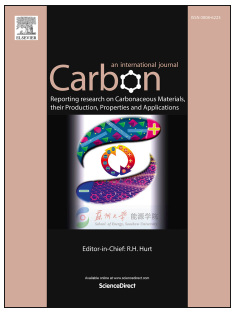


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# Influence of the oxygen-containing surface functional groups in the methane hydrate nucleation and growth in nanoporous carbon

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## Abstract

Petroleum pitch-derived activated carbon (PP-AC) has proved to be an excellent platform to promote the methane hydrate formation in milder condition than nature, even though the water-to-hydrate yield at the threshold formation pressure of 3.3 MPa is rather low (ca. 13 %). Herein, we report that the presence of oxygen-containing surface functional groups in the oxidized carbon analogue (PP-AC_Ox) plays a significant role in the nucleation and growth in the low-pressure region. High-pressure methane adsorption/desorption isotherms revealed an enhancement in the water-to-hydrate yield up to *ca*. 51 % around 3.3 MPa and 2 ºC, in an extremely narrow working pressure window, with no hysteresis associated.

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Methane hydrates (MHs) are crystalline solids that are formed in deep-water marine environments and in the permafrost under thermodynamically favorable conditions. Artificial MHs are an outstanding alternative to store natural gas [1]. Unfortunately, storing methane *via* wet strategy is not an easy task. Several approaches have been tested in order to increase the gas-liquid contact area, and consequently the rate of MH formation [2-4]. In this context, petroleum pitch-derived activated carbon (PP-AC) has successfully demonstrated to be an excellent platform able to host and promote the synthesis of MH [5]. Taking into account that in these systems the methane molecules are trapped in cavities formed by hydrogen-bonded water molecules (sI structure $CH_4.5.75H_2O$) [2], the presence of a certain surface chemistry able to interact with the water molecules must exert an influence in the MH formation process, either positive or negative [6]. Therefore, herein we report the influence of oxygen-containing surface functional groups in the formation/dissociation process of confined MHs using an oxidized petroleum pitch-derived activated carbon as a host structure (PP-AC_Ox).

In order to incorporate a rich surface chemistry on the carbon surface (oxygen surface groups), the original PP-AC was immersed into a $H_2O_2$ (5M) solution for 2 h at ambient temperature. After the oxidation treatment, the newly created functional groups give rise to a slight blockage of the total porosity, i.e. total pore volume goes down from 2.54 $cm^3/g$ in PP-AC to 2.12 $cm^3/g$ in PP-AC_Ox. The micropore volume ($V_{N2,DR}$) decreases from 1.24 $cm^3/g$ in PP-AC to 0.95 $cm^3/g$ in PP-Ox, while the narrow micropore volume ($V_{CO2,DR}$) remains almost unaffected, 0.28 $cm^3/g$ (Table 1, Figure S1). Further information about pore size distribution can be extracted after applying Quenched Solid Density Functional Theory (QSDFT) method (slit-shaped pore) to the nitrogen adsorption data at -196 ºC. Figure S2 exhibits a bimodal distribution and confirms the fact that pores below *ca* 1.5 nm are almost unaffected by the oxidation treatment (in close agreement with $CO_2$ adsorption isotherm data), while wide micropores/narrow mesopores (above 1.5 nm) are slightly blocked. Taking into account the pore volume and the water uptake from the water adsorption isotherms (more

details in Supporting information, Figure S3) [7], PP-AC_Ox sample will be evaluated in the methane hydrate formation process using three different water loadings Rw=2 (saturated sample), and Rw=4.1 and 6.0 (oversaturated samples).

Figure 1 (a) shows the high-pressure methane adsorption/desorption isotherms for the oxidized sample at 2 ºC after pre-humidification with different water contents. The methane adsorption capacity of the dry carbon and bulk water are also reported for the sake of comparison. PP-AC_Ox sample saturated with water (Rw= 2) shows a drastic decrease in the methane uptake compared to the dry sample. Two conclusions arise from these observations: 1) pores are blocked by pre-adsorbed water so that gas molecules cannot be adsorbed, and 2) the water-to-hydrate yield is very low even at high pressures. Apparently, the presence of large water-surface interactions in the oxidized carbon inhibits the hydrate formation process. These findings are in close agreement with previous studies from our research group using metal-organic frameworks with different surfaces nature [6]. To give some light into the nature of the oxygen surface groups in sample PP-AC_Ox, temperature-programmed decomposition (TPD) and X-ray photoelectron spectroscopy (XPS) measurements were performed.

TPD results and C/O atomic ratio calculated by dividing the area under C 1s peak with that of O 1s peak of the XPS for the original and oxidized samples are summarized in Table 1 (further details are giving in supporting information Figure S4 and Figure S5, respectively). Compared to the original sample, PP-AC_Ox gives rise to almost a fourfold increase in the number of $CO_2$ molecules evolved and a twofold increase for evolved CO molecules in TPD experiments. The XPS analysis confirms the increment of oxygen-containing functional groups with a C/O value of 10.9 in PP-AC_Ox compared to 17.8 in the original PP-AC. On the basis of TPD and XPS analysis it can be concluded that the oxidation treatment with $H_2O_2$ incorporates mostly carboxylic and anhydride groups (a deep analysis is presented in SI). It is important to mention that the oxidation process selected was rather weak since using stronger

oxidizing agents would deteriorate the sample. These oxygen-containing functional groups give a more hydrophilic in nature carbon surface [8] capable to modify the hydrogen bonding between the carbon surface and the adsorbed water molecules through stronger water-surface interactions, with the associated changes in the methane hydrate formation process.

Indeed, the scenario changes drastically when the oversaturated PP-AC_Ox sample (Rw=4.1) is exposed to methane at high pressure. Interestingly, at the threshold pressure of 3.3 MPa the methane adsorption isotherm reveals a sharp vertical jump in the adsorption capacity up to a value of 20 mmol/g. Thereafter the system reaches a plateau with a scarce enhancement in the methane adsorption capacity. Interestingly, no hysteresis loop can be appreciated. This behavior reflects that the adsorption process occurs in thermodynamic equilibrium conditions [1] and in a time-scale of minutes, i.e. short induction time (nucleation periods), *ca.* 15 minutes (Figure 1(b)). This result is crucial for a constant energy-supply and a quick charge/discharge device in a hypothetical on-board natural gas storage system via a wet strategy.

Considering the stoichiometry of the methane hydrate sI (1 molecule of $CH_4$ per 5.75 molecules of $H_2O$), the yield of MH in the system can be easily calculated considering the methane adsorption capacity at a given pressure. Sample PP-AC_Ox pre-humidified with Rw= 4.1 adsorbs 20 mmol/g dry carbon (i.e. 20 mmol $CH_4$ in 4.1g $H_2O$) at 3.3 MPa, thus giving rise to a water-to-hydrate yield of *ca*. 51 %. This value is much higher than the yield achieved with the original PP-AC (only 13 % of the water is forming MH crystals at the same conditions (see Figure S6)). These findings clearly anticipate a different distribution of the pre-adsorbed water in the original and oxidized sample. While in the original activated carbon water must be randomly distributed over the whole porosity (micro and mesopores must be filled) due to the hydrophobic nature of the carbon surface, in the oxidized material water must preferentially nucleate at the oxygen surface functionalities. Previous studies described in the literature [7] have shown that oxygen surface groups act as nucleation centers for water

clustering. Taking into account that oxygen functionalities grow preferentially in surface defects and in the pore mouth, one would expect a different distribution of water molecules and consequently a different performance towards the methane hydrate process depending on the surface chemistry. Taking a look at the experimental data of the original PP-AC sample (Figure S6), there was a clear difference between methane hydrate formation in large cavities, taking place at medium pressure (around 3-4 MPa), and kinetically restricted methane hydrate formation in small cavities (mesopores and micropores) that require larger pressures [5]. From these premises, the preferential location of water clusters in the large cavities and pore mouth in the oxidized carbon must be responsible for the shift observed in the hydrate formation process to lower pressures, in close agreement with the results described in Figure 1. A further increase in the total pressure above 4 MPa does not give rise to additional methane hydrate formation, i.e. the remaining water (49 %, which is equivalent to the sample with Rw= 2 $gH_2O/g$) is not prone to participate in the methane hydrate formation process. A further increase in the amount of pre-adsorbed water to Rw=6 gives rise to a shift to a higher threshold pressures before the hydrate formation starts and a decay in the total hydrate yield. Furthermore, the methane hydrate formation process is associated with a certain hysteresis loop. At this stage, it is important to note that bulk water exhibits no methane adsorption over the whole pressure range evaluated. Interestingly, the original and oxidized samples display similar methane adsorption isotherms in dry conditions (Figure S6), this behavior is quite predictable since the methane molecules (kinetic diameter 0.38 nm) are adsorbed preferentially in micropores with *ca* 0.8-1.1 nm in size [9], which are almost unaffected by the oxidation treatment, as was discussed above.

Because the nucleation and growth of synthetic methane hydrate is highly sensitive to temperature and pressure, especially around the freezing point of water [4], small changes in the adsorption temperature system were also tested. Figure 2 represents the high-pressure methane isotherms at 0, 2 and 5 ºC for PP-AC_Ox (Rw=4.1). There is almost no difference in

the threshold pressure for the nucleation at 0 and 2 ºC (3.3 MPa), while at 5 ºC a larger pressure *ca.* 5.5 MPa is required to initiate the crystallization process. The dissociation pressure shows a small delay of 0.2 MPa compared to the nucleation pressure for the system at 0 ºC (3.1 MPa), nil displacement for 2 ºC (both nucleation and dissociation are in equilibrium) and a larger hysteresis of 1 MPa at 5 ºC (4.5 MPa). The dissociation conditions are in agreement with the reported bulk system in the literature [1]. The differences in the formation pressure can be attributed to the water phase. At 0 ºC the water in large cavities must be in a solid-like phase, whereas at 5 ºC the water must still be a liquid. Ice or cold water have a tendency to maintain a more ordered structural arrangement owing to limited molecular activity compared to liquid-phase water [10]. Then, the activation energy for reorganizing ice into hydrate is probably less than the activation energy required to reorganize liquid water into hydrate.

Interestingly, at the three temperatures evaluated the yield in the first step is rather similar (*ca.* 50%). However, the isotherm performed at 0 ºC exhibits a second increment in the methane uptake at pressure close to 6 MPa. Apparently, once overcoming the interaction barriers between the water molecules and the oxygenated functional groups at the large cavities and in the entrance of the pores, the previous unavailable water molecules of water starts to participate in the reaction. Consequently, further methane hydrate crystals can formed, which enhances the MH-yield up the value of 80 % at 10 MPa.

To summarize, the oxidation treatment makes possible to increment the MH-yield up to 51 % for sample PP-AC_Ox at the formation pressure of 3.3 MPa and 2 ºC comparing to the original sample. This yield can be increment up to 80% at 0 ºC and 10 MPa. These results are very promising for gas storage and transportation since storing natural gas in solid form is safer than the compressed natural gas (20 MPa) and cheaper than liquefied natural gas (-162 °C). However, the optimum conditions (pressure and temperature) have to be determined

for any given application according to a deep evaluation in terms of safety, economic-saving, and efficiency.

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## Figures and Tables

**Table 1.** Textural and surface characteristic of samples

| **Textural Properties** | | | | |
|---|---|---|---|---|
| | $S_{BET}$ $m^2/g$ | $V_{t,0.95}$ $cm^3/g$ | $V_{N2,DR}$ $cm^3/g$ | $V_{CO2,DR}$ $cm^3/g$ |
| PP-AC | 3760 | 2.54 | 1.24 | 0.29 |
| PP-AC _Ox | 2990 | 2.12 | 0.95 | 0.28 |
| **Functional groups information** | | | | |
| | $CO_2$ μmol/g | CO μmol/g | $H_2O$ μmol/g | C/O (XPS) |
| PP-AC | 235 | 807 | 443 | 17.8 |
| PP-AC _Ox | 814 | 1774 | 6491 | 10.9 |

$S_{BET}$, $V_{t,0.95}$ and $V_{N2,DR}$ are calculated from the $N_2$ adsorption isotherm data at -196 ºC and represent the total pore volume and micropore volume, respectively. $V_{CO2,DR}$ is calculated from the $CO_2$ adsorption isotherm data at 0 ºC and represents the narrow micropore volume.

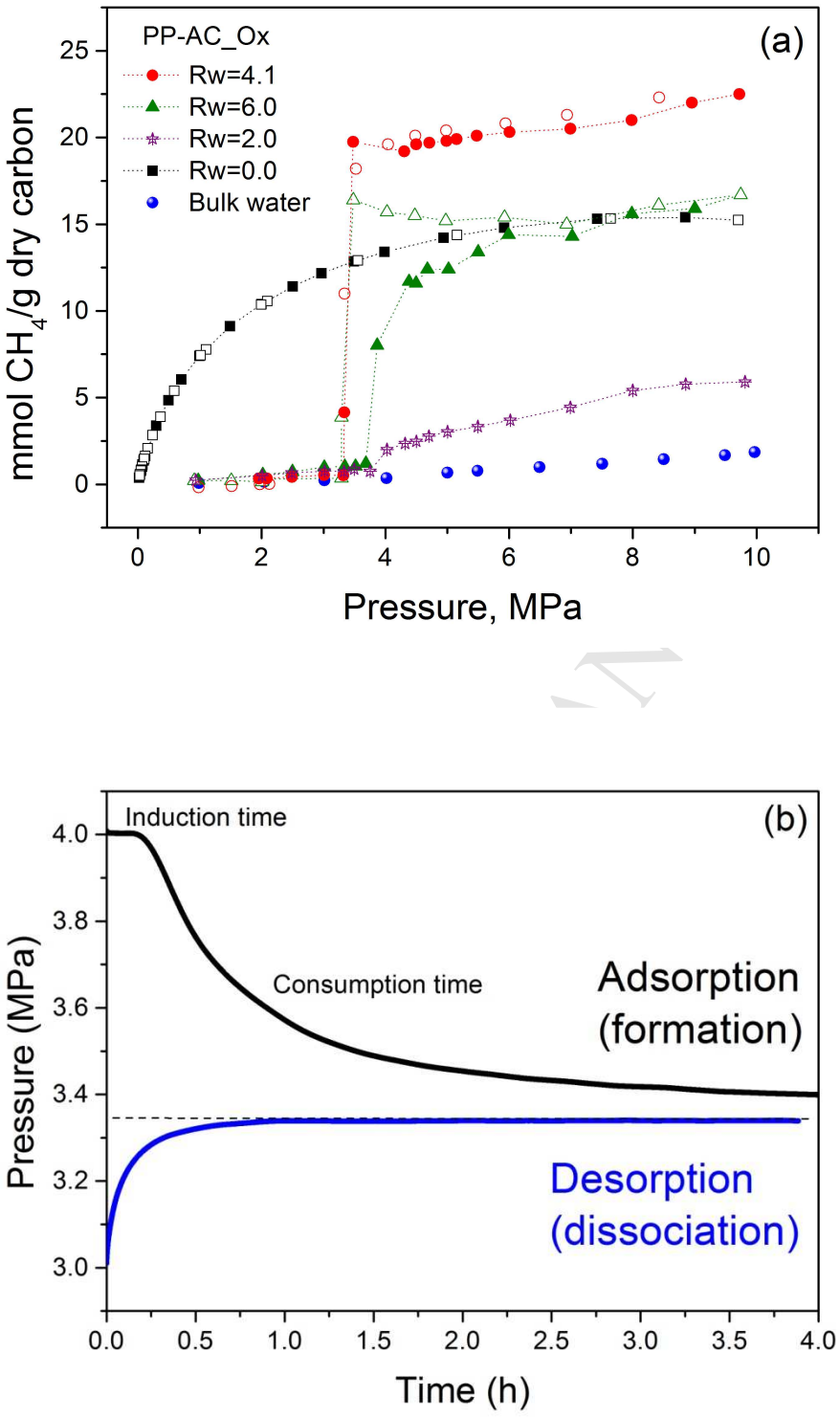


*Figure 1*. (a) High-pressure methane adsorption isotherms at 2 ºC for PP-AC_Ox with different loading water, Rw =2, 4.1, 6 g $H_2O$ /g dry carbon. Dry PP-AC_Ox and bulk water are also represented for comparative purpose; (b) P-time curve for PP-AC_Ox_Rw=4.1 point 3.3 MPa.

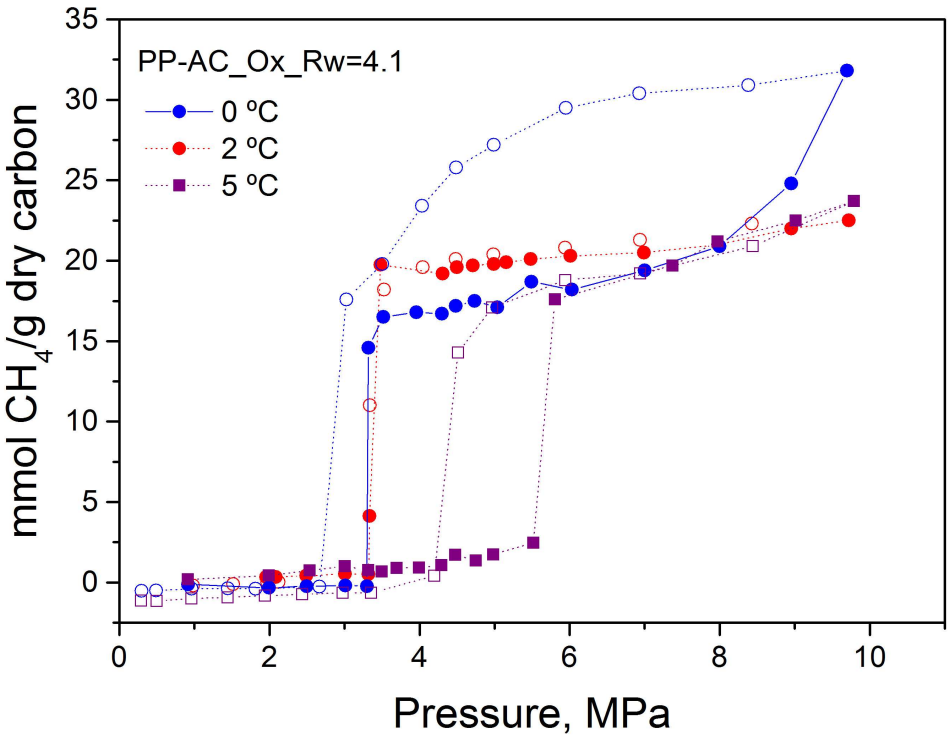


*Figure 2*. Effect of the temperature in methane hydrates formation. High-pressure methane adsorption isotherms for PP-AC_Ox_Rw=4.1 at 0, 2 and 5 ºC.